



Evidence for Epoxide Formation from the Electrochemical Reduction of Ethylene Carbonate

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It is now generally agreed that the electrochemical reduction of ethylene carbonate (EC) plays an important role in the formation of an effective solid electrolyte interface layer on the carbon anode in lithium-ion cells. However, neither the composition of this layer nor the reaction pathways involved in its formation have been clearly established. We report reflectance infrared spectra from a glassy carbon electrode surface after EC/tetrahydrofuran electrolyte reduction that is unlike any other we have seen in the literature. The spectrum has its strong absorption peak at 838 cm^{-1} , and this feature is clearly shown not to be from the monoethylcarbonate lithium salt. Ethylene oxide is suggested as a possible, but not exclusive, reduction product. The suggested reaction pathway is an electrochemical-chemical sequence, electrochemical reduction of water to form hydroxide, and hydroxide addition to form ethylene oxide and lithium bicarbonate.

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As the negative electrode in a Li-ion battery is charged to voltages near the lithium metal potential, one or more of the components of the electrolyte may be reduced, particularly so on the first or "formation" charge. Ideally, the products from this reduction form a solid electrolyte interface (SEI) on the electrode surface, and prevent further reduction of the electrolyte while still allowing Li^+ transport.¹ The SEI layer can come from reduction of either the solvent, typically an aprotic organic solvent, the salt, or from an additive specifically developed for this purpose. There are, therefore, many variables to be accounted for in a study of the chemistry of the SEI layer, and its composition may be expected to vary with different battery chemistries.

Ethylene carbonate (EC) is a widely used solvent in electrolytes specifically for the Li-ion battery, presumably because its reduction contributes to the formation of an effective SEI layer on the graphite electrode. A frequently proposed chemistry is that the electrochemical reduction of EC begins at potentials >1 V, the potential where Li^+ intercalation into graphite begins.^{1,2} The products from the initial reduction of EC prevent solvent cointercalation. Further reduction may occur as the graphite is fully charged to close to the lithium metal potential, which may include reduction of the salt as well. The details of this reduction chemistry are, however, still highly debated subjects.³ The reduction products most frequently proposed include lithium ethyl carbonate, lithium carbonate, and ethylene gas.^{4,5} In this paper, we report the finding of a reduction product containing an epoxide ring during the electrochemical reduction of ethylene carbonate (EC) on a glassy carbon anode surface. To the best of our knowledge this finding has not been previously reported.

Experimental

Materials.—Propylene oxide (Fluka, 99.5%), tetrahydrofuran (THF) (J. T. Baker, H_2O content less than 0.003%), EC (Grant Chemical, less than 20 ppm H_2O), and LiClO_4 (EM industries) were used as received without further purification. The electrolyte employed was EC (5 mM) in THF with 0.1 M LiClO_4 .

Electrochemical and infrared (IR) studies.—A single compartment cell with three electrodes was assembled for the electrochemical experiments and placed in a He atmosphere glove box. Lithium metal was used for both counter and reference electrodes. Cyclic voltammetry was conducted using an EG&G model 273 potentiostat. Two types of working electrodes were employed: a small gold electrode (1 mm radius) was selected for the cyclic voltammetry (CV) experiments, while a larger glassy carbon electrode

(1×1 cm) was used for the Fourier transform infrared (FTIR) studies. The electrodes were polished with 0.3 and 0.05 μm alumina powder prior to use. With either electrode material, the open-circuit potential was *ca.* 2 V. The glassy carbon electrode was held at the EC reduction potential for 5 min then brought back to 2 V. After the electrochemical experiment, the electrode was removed from the cell and inserted into an airtight IR cell fitted with a KBr window. Because the IR geometry can influence the relative intensity of different vibrations, *e.g.*, specifically transmittance vs. reflectance spectra, all IR spectra, even those for the reference compounds, were obtained in the reflectance mode. Reference compounds, either pure liquids or salts dissolved in THF, were placed on a glassy carbon or gold substrate, and placed in the same IR sample holder. The IR spectra were collected using a Nicolet Magna 760 spectrometer fitted with a Nic-Plan IR microscope. Diffuse scattering reflectance geometry was used with a Schwarzschild objective.

Synthesis and characterization of monoethylcarbonate, lithium salt.—Lithium ethylcarbonate was synthesized following the general procedure of Behrendt.⁶ Ethanol (Burdick and Jackson HPLC grade) was dried over K_2CO_3 and under argon atmosphere for 1 night. It was freshly distilled and immediately transferred to a glove box. Lithium metal and dry CO_2 were used without further purification.

A 250 mL reaction flask with a glass stopcock septum sidearm, 14/20 ground glass bent adapter with glass stopcock, and Teflon stir bar were dried overnight in a 115°C oven. Upon removal from the oven all glassware was transferred to a glove box. Approximately 50 mg (7.1 mmol) lithium metal was placed in the flask and 50 mL of EtOH was added dropwise over 30 min. Gas bubbles were observed as the reaction proceeded. After all of the lithium had reacted, a clear, colorless solution remained. The flask was sealed, taken out of the glove box, and attached to a Schlenk line. An argon line was attached to both the sidearm and the adaptor and argon flow started. The argon flow was increased and crushed CO_2 (Dry Ice) was spooned in over the course of 2 h. After CO_2 addition, a clear, colorless solution remained. The mixture was poured into a beaker and diethyl ether was added until the solution became cloudy. White crystals formed upon cooling to 0°C. The crystals were collected via vacuum filtration. Total collected was 0.55 g-5.7 mmol-80% yield).

Results and Discussion

According to the recent literature report from Paolucci *et al.*⁷ THF is not reduced on an inert electrode before the deposition of lithium metal. LiClO_4 was selected as the salt rather than LiPF_6 due to its relative stability against reduction. Therefore, THF/0.1 M LiClO_4 was used as the supporting electrolyte in all experiments. The CV of Au in the supporting electrolyte is shown in

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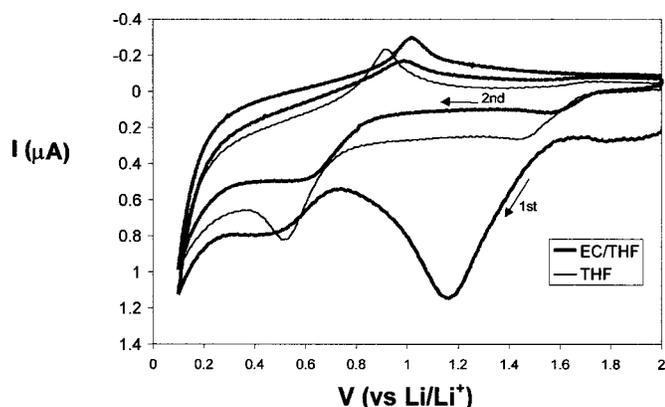


Figure 1. CV of a Au electrode in 0.1 M $\text{LiClO}_4/\text{THF}$; (thin line) base voltammetry, (dark line) with 5 mM EC. 20 mV/s.

Fig. 1. The irreversible peak at *ca.* 11.6 V is assigned to water reduction, and the quasi-reversible peaks centered about 0.7 V (± 0.2) correspond to the underpotential deposition and consequent stripping of Li on Au.⁸ After addition of EC to 5 mM, the first cathodic sweep changes dramatically, with a significant irreversible reduction process occurring with a half-wave potential of *ca.* 1.4 V. On the second cathodic sweep, the current drops back close to the baseline current for the supporting electrolyte, indicating the electrode surface is no longer active for EC reduction. The irreversible reduction process is assigned to electrochemical reduction of EC, forming a passivating product layer on the Au surface. Interestingly, Li underpotential deposition (UPD) still occurs through the passive film, although the process is now less reversible. Some additional solvent reduction may, however, also occur at potentials below 0.3 V.

Reduction of the electrolyte EC/THF- LiClO_4 shows a broad and weak peak at 1640 cm^{-1} (Fig. 2b). This is the feature most discussed in previous studies of carbonate solvent reduction using FTIR, and was taken as the key indicator of the formation of a lithium alkyl carbonate. The peak at 838 cm^{-1} has, however, the highest intensity in our spectrum and is absent in the electrolyte before reduction. A peak at a similar position ($830\text{--}850\text{ cm}^{-1}$) was also observed in other IR studies of alkyl carbonate reduction, but

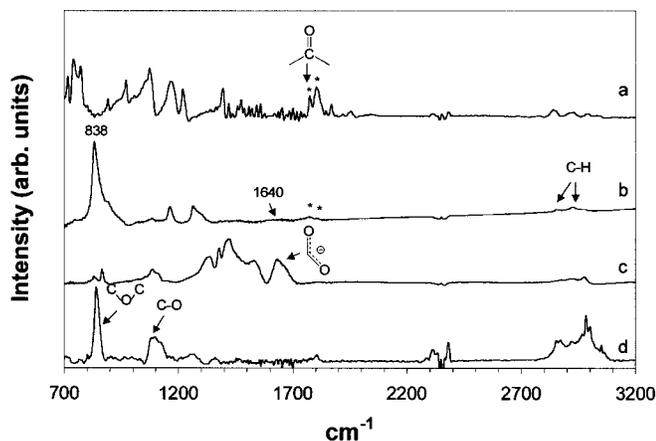
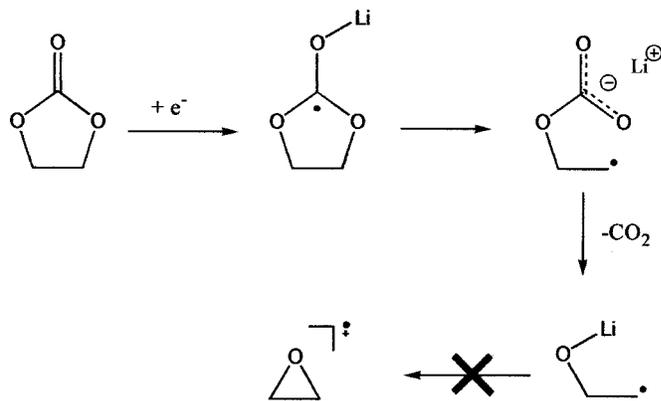


Figure 2. Reflectance IR spectra from (a) a glassy carbon electrode emersed from the 1.0 M $\text{LiClO}_4/\text{THF}$ -5 mM EC solution without application of a potential to the electrode, (b) after polarization at 50 mV for 5 min, (c) a clean glassy carbon electrode onto which a thin layer of lithium monoethylcarbonate in ethanol solution has been applied, and (d) a clean glassy carbon electrode onto which a thin layer of propylene oxide has been applied. (* peaks are from C=O stretching of EC).

was much weaker than here.^{4,9} It was ascribed to the bending mode of a lithium alkyl carbonate following the work of Behrendt *et al.*,⁶ who originally suggested this assignment to their transmittance IR spectra of alkali metal salts of monoalkyl carbonates. Figure 2c shows the reflectance IR spectrum of the monoethylcarbonate lithium salt dissolved in ethanol, as synthesized in this study. The relative intensities of the fundamental vibrations assigned to the lithium alkylcarbonate in this reflectance spectrum are different from those in the transmission spectrum of Behrendt *et al.*⁶ In contrast to the reduction product, the carbonate C=O stretching absorption around 1640 cm^{-1} is of medium intensity, but the absorption peak at 831 cm^{-1} is very weak. It is clear from these results that the peak at 838 cm^{-1} in Fig. 2b does not come from lithium alkylcarbonate. Interestingly, this feature exists in all reductions carried out in the range from 50 mV to 1.8 V (vs. Li/Li^+). No reduction of the electrolyte, however, was observed above *ca.* 2 V.

Another functional group that has strong absorbance near $800\text{--}900\text{ cm}^{-1}$ is an epoxide ring. The C-O-C asymmetric stretching of epoxides occurs in the region of 840 cm^{-1} and has a strong absorption cross section.¹⁰ The IR reflectance spectrum from pure propylene oxide is shown in Fig. 2d for reference purposes. The frequency of the C-O-C stretching absorbance in this sample is virtually identical to that seen in the EC reduction products. We propose, therefore, that the strong absorption peak at 838 cm^{-1} in the IR spectrum of the electrode surface after EC reduction is from an epoxide ring. Ethylene oxide, dissolved in the electrolyte which adheres to the electrode upon emersion (no rinsing was used), is a possible candidate. Although ethylene oxide is a gas at room temperature (bp 13.2°C) it is readily soluble in a variety of organic solvents.¹¹ In THF it is often used as a feedstock for polymer synthesis.¹²⁻¹⁴ A higher molecular weight polymeric epoxide adhering to the electrode surface is also a possibility.

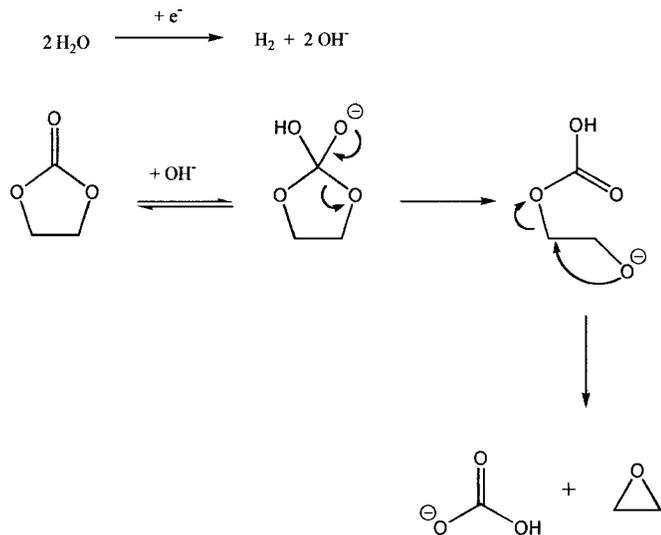
In the following discussion we consider possible mechanisms for the formation of ethylene oxide from the electrochemical reduction of EC. EC can be synthesized from ethylene oxide and CO_2 .¹⁵ It therefore seems logical to consider a direct retrosynthesis from EC to ethylene oxide. Formation of the epoxide ring from the five membered framework of EC has much literature precedence. A patent by Teles *et al.* outlines the synthesis of glycidol (an epoxide) from glyceryl carbonate (an EC derivative) in one step using salts of alkali metals and heat.¹⁶ In organic synthesis reactions involving nucleophilic attack on a carbonate are used to generate an ethylene glycol derivative. Modification of the glycol product followed by base addition yields the epoxide moiety.¹⁷⁻²⁰ On the other hand, it is not immediately obvious that there is a direct electrochemical reduction pathway from EC to an epoxide ring. A single electron transfer to EC to create a radical anion (Scheme 1)



Scheme 1.

does not have a simple pathway to an epoxide ring. A possibility is a bridged radical intermediate and subsequent loss of one electron. Bridged radical species have been reported but the bridging atom of these compounds has been bromine.²¹ We are not aware of the oxy-

gen atom being able to bridge in this fashion and probe calculations of the ethoxide radical anion at the HF/3-21g* level show no bridging. A clue to the mechanism of epoxide formation lies in the experimental observation that the 838 cm⁻¹ absorption peak was found in a sample that was held at a reduction potential as high as 1.8 V for 5 min. As we stated above, the reduction at 1.8 V is generally ascribed to the reduction of H₂O to form H₂ gas and OH⁻. It is possible that the epoxide forms from hydroxide ion addition to EC, with the hydroxide formed by electrochemical reduction of water. The reaction sequence is shown in Scheme 2.



Scheme 2.

Degradation of the tetrahedral intermediate from OH⁻ addition could lead to ethylene oxide and a salt of carbonic acid (lithium bicarbonate). It should be mentioned that a second molecule of OH⁻ could add to the carbonyl group and form ethylene glycol. A large amount of OH⁻, however, would be needed for the second addition to occur. We note that ethylene glycol was observed by Zhang *et al.*²² in the electrolyte of cycled "commercial" lithium-ion cells that contain larger amounts of water than in the research cells used here. Further study of the mechanism of epoxide formation, *e.g.*, addition of D₂O to the electrolyte and the resulting effect on the vibrational spectra, are in progress.

Conclusion

Reflectance infrared spectra from a glassy carbon electrode surface after EC/THF electrolyte reduction give a strong absorption

peak at 838 cm⁻¹. The spectra are essentially identical for all reduction potentials from 50 mV to 1.8 V (*vs.* Li/Li⁺). The spectra are different than those of monoethylcarbonate lithium salt and unlike any other we have seen in the literature. Epoxides have strong absorbance in the same region, and the IR spectrum of propylene oxide bears strong resemblance to that of the EC reduction products. Ethylene oxide is suggested as a possible reduction product. The suggested reaction pathway is an electrochemical-chemical sequence, electrochemical reduction of water to form hydroxide, and hydroxide addition to form ethylene oxide and lithium bicarbonate.

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References

1. M. Winter, J. O. Besenhard, M. E. Spahr, and P. Novak, *Adv. Mater.*, **10**, 725 (1998).
2. (a) A. Naji, P. Willmann, and D. Billaud, *Carbon*, **36**, 1347 (1998); (b) A. Naji, J. Ghanbaja, P. Willmann, and D. Billaud, *Carbon*, **35**, 845 (1997).
3. Y. Ein-Eli, *Electrochem. Solid-State Lett.*, **2**, 212 (1999).
4. D. Aurbach, Y. Ein-Eli, O. Chusid, Y. Carmeli, M. Babai, and H. Yamin, *J. Electrochem. Soc.*, **141**, 603 (1994).
5. Z. X. Shu, R. S. McMillan, and J. J. Murray, *J. Electrochem. Soc.*, **140**, 922 (1993).
6. V. W. Behrendt, G. Gattow, and M. Drager, *Z. Anorg. Allg. Chem.*, **397**, 237 (1973).
7. F. Paolucci, M. Carano, P. Ceroni, L. Mottier, and S. Roffia, *J. Electrochem. Soc.*, **146**, 3357 (1999).
8. D. Aurbach, M. L. Daroux, P. W. Faguy, and E. Yeager, *J. Electrochem. Soc.*, **134**, 1611 (1987).
9. S. Mori, H. Asahina, H. Suzuki, A. Yonei, and K. Yokoto, *J. Power Sources*, **68**, 59 (1997).
10. E. Pretsch, T. Clerc, J. Seibl, and W. Simon, in *Tables of Spectral Data for Structure Determination of Organic Compounds*, Springer-Verlag, Berlin, p. 190 (1989).
11. *CRC Handbook of Chemistry and Physics*, 74th ed., D. R. Lide, Editor, p. 3, CRC Press, Boca Raton, FL (1993).
12. A. Bar-Ilan and A. Zilkha, *J. Macromol. Sci., Chem.*, **4**, 1727 (1970).
13. A. Deffieux, E. Graf, and S. Boileau, *Polymer*, **22**, 549 (1981).
14. H. Reuter, S. Hoering, and J. Ulbricht, *Eur. Polym. J.*, **25**, 1113 (1989).
15. L. Vogdanis and W. Heitz, *Makromol. Chem., Rapid Commun.*, **7**, 543 (1986).
16. J. H. Teles, N. Rieber, and W. Harder, U.S. Pat. 5,359,094 (1994).
17. T. Kazunobu, M. Misawa, K. Ohta, K. Tasuta, and M. Kinoshita, *Tetrahedron Lett.*, **30**, 6417 (1989).
18. S. Nishiyama, Y. Ikeda, S. Yoshida, and S. Yamamura, *Tetrahedron Lett.*, **30**, 105 (1989).
19. G. W. J. Fleet and P. W. Smith, *Tetrahedron*, **43**, 971 (1987).
20. G. W. J. Fleet and P. W. Smith, *Tetrahedron Lett.*, **26**, 1469 (1985).
21. P. S. Skell and K. J. Shea, in *Free Radicals*, J. Kochi, Editor, p. 809, Wiley, New York (1973).
22. X. Zhang, P. N. Ross, Jr., R. Kostecki, F. Kong, S. Sloop, J. B. Kerr, K. Striebel, E. Cairns, and F. McLarnon, *J. Electrochem. Soc.*, **148**, A463 (2001).